EFFECTS OF CATALYST PROMOTERS ON THE GROWTH OF SINGLE-LAYER CARBON NANOTUBES

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ABSTRACT

The discovery of a catalytic route to the growth of single-layer carbon nanotubes suggests that it may be possible to produce these materials with better selectivity and in higher yield[1,2]. Increasing the production efficiency is essential for characterization and application of these materials. We have discovered several catalyst promoters, in particular S, Bi, and Pb, that greatly enhance the single-layer carbon nanotube yield, and extend the distribution of nanotube diameters to much larger sizes (> 3 nm). Co crystallites encapsulated in graphitic polyhedra also form abundantly when S, Bi, or W is present. Understanding these catalytic process is of substantial scientific and technological importance.

CARBON NANOTUBES

The term "carbon nanotube" generally refers to carbon with a cylindrical graphene structure. Multilayer carbon nanotubes are generally produced on the cathode tip deposit in an electric arc[3]. These nanotubes are typically composed of 2 to 50 layers of cylindrical shells, with tube diameters ranging from several to several tens of nm. Single-layer carbon nanotubes can be produced with or without a catalyst. Carbon can self-assemble into tubes without a catalyst by either hydrocarbon decomposition[4] or carbon vapor condensation[5] on a substrate surface. The yield is low and the nanotubes produced usually have more than one layer. On the other hand, catalytic synthesis of carbon nanotubes produces nanotubes exclusively with a single layer and in higher yields. Fe, Co, and Ni catalyze the growth of single-layer carbon nanotubes when co-vaporized with carbon in an arc[1,2,6,7]. The nanotubes produced have a very high aspect ratio (length to diameter), and have diameters from subnanometer to several nanometers and lengths from hundreds of nm to μm. Metals such as Y and Gd have also been shown to catalyze nanotube growth[8,9]. These tubes, however, are rooted on a metal carbide (or metal oxide) crystal, and have diameters ranging from 1 to 2 nm and lengths from 10 to 200 nm. This article focuses on the single-layer carbon nanotubes produced using Co catalyst, and the effects of certain catalyst promoters on the nanotube growth.

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CATALYTIC SYNTHESIS OF SINGLE-LAYER CARBON NANOTUBES

We produce nanotubes with an electric arc, using a dc current of 95 A with a supply voltage of 25 V, under 300 to 500 Torr helium. The cathode is a 6 mm graphite rod, and the anode is a graphite rod cored at the center and filled with a mixture of C, Co, and additives such as S, Bi, Pb, and W. The metal concentration is 4 atomic % Co and an equal amount (in atomic %) of the additive is used. We sonicate the soot in ethanol and place drops of the solution containing suspended materials on a holey carbon grid for transmission electron microscopy (TEM) study.

EFFECTS OF CATALYST PROMOTERS

We found that S, Bi, and Pb enhance the single-layer carbon nanotube yield in the presence of Co, yet they do not catalyze tube growth when used without the catalyst. Therefore they behave as catalyst promoters. Figure 1a is a typical TEM image of the soot containing nanotubes, metal particles, fullerenes, and non-crystalline carbon. Bundles consisting of hundreds of single-layer nanotubes are frequently observed. The density of nanotubes is very high and large diameter (> 2 nm) single-layer nanotubes are abundant, as shown in Figure 1b. High resolution TEM images show that Co particles encapsulated in graphitic polyhedra are produced in good yields with the use of S or Bi (see Figure 2)[10].

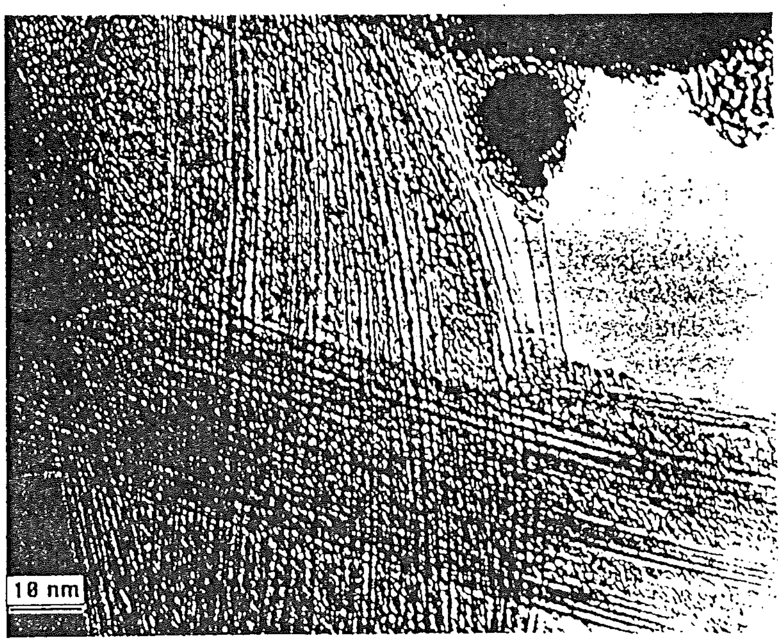

Figure 1 Transmission electron micrograph of soot produced by vaporizing Co, Bi, and C by using an arc (see text). The large dark objects shown in the figure are pure Bi particles, and the smaller spots are *fcc* Co crystals, as determined with energy dispersive spectroscopy (EDS) and high resolution TEM images.

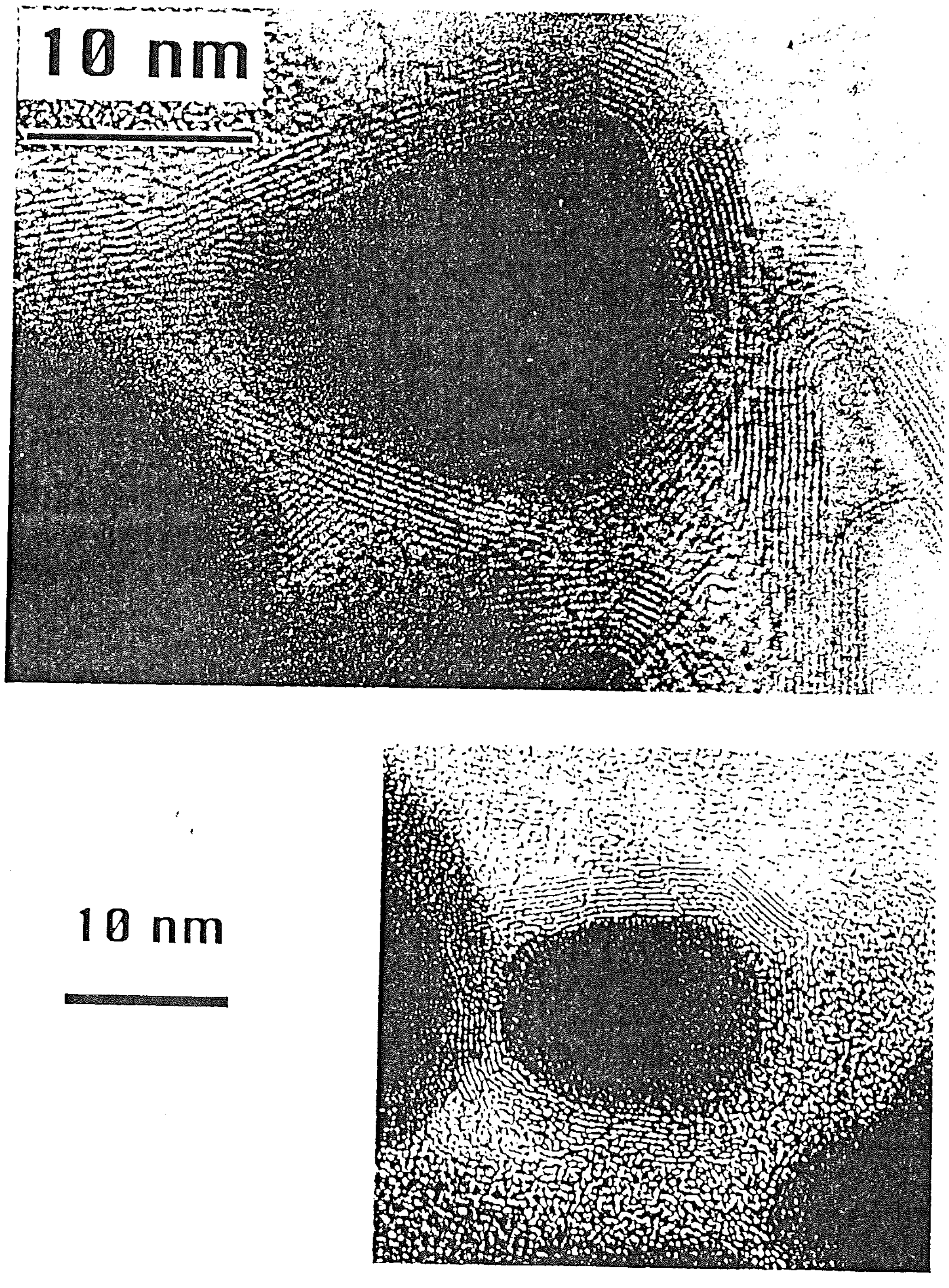

Figure 2 Co crystals encapsulated in graphitic polyhedra, produced with (a) S and (b) Bi.

DISCUSSION

The nanotube diameter distribution has been modified by the promoters, as it contains tubes of sizes not observed when Co is used alone. We measured diameters of over 150 tubes for each sample from high resolution TEM micrographs, and the resulting histogram is shown in Figure 3. The ranges of the nanotube diameters are 1 to 4 nm, 1 to 5 nm, and 1 to 6 nm, for tubes produced using promoters Pb, Bi and S, respectively, compared to 1 to 2 nm when using Co alone.

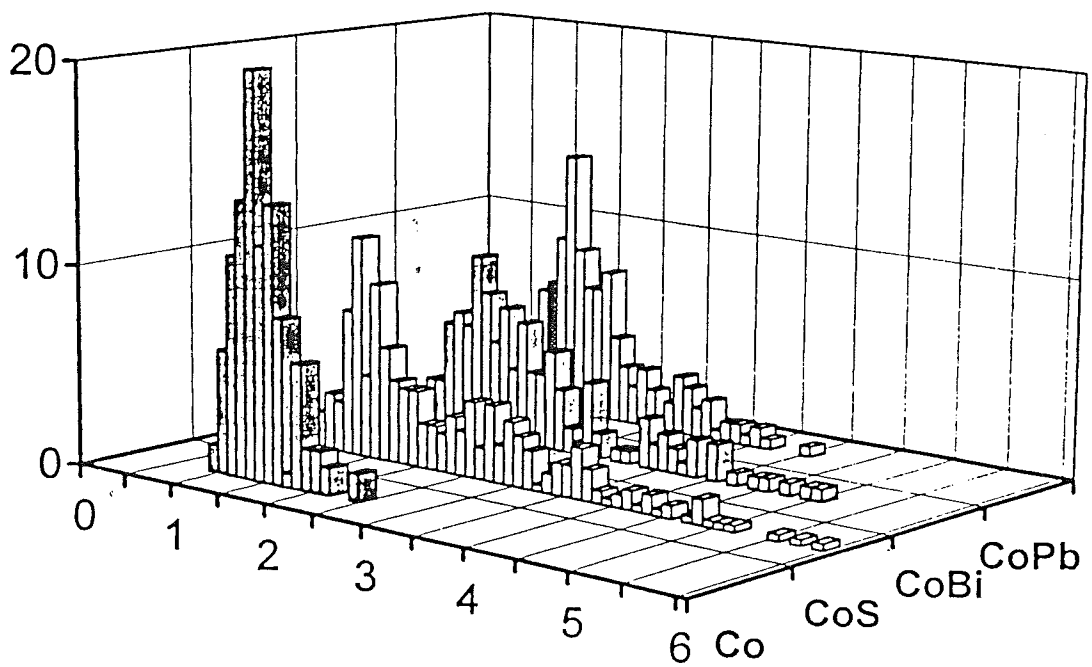

Figure 3 Histogram of nanotube diameter distribution of samples made from catalyst Co, Co+S, Co+Bi, and Co+Pb. The numbers of tube diameters measured were more than 150 for Co, 300 for Co+S, 150 Co+Bi, and 200 for Co+Pb. There is 10 % uncertainty in the measured diameters, and we expect larger fluctuations in diameters for tubes larger than 2 nm due to the radial deformation.

We have also tested another heavy metal, W, and found that it reduces the nanotube yield. Additionally, the tubes produced have diameters between 1 and 2 nm. To our surprise, however, W does enhance the graphitization of the carbon surrounding the Co crystallites, as shown in Figure 4.

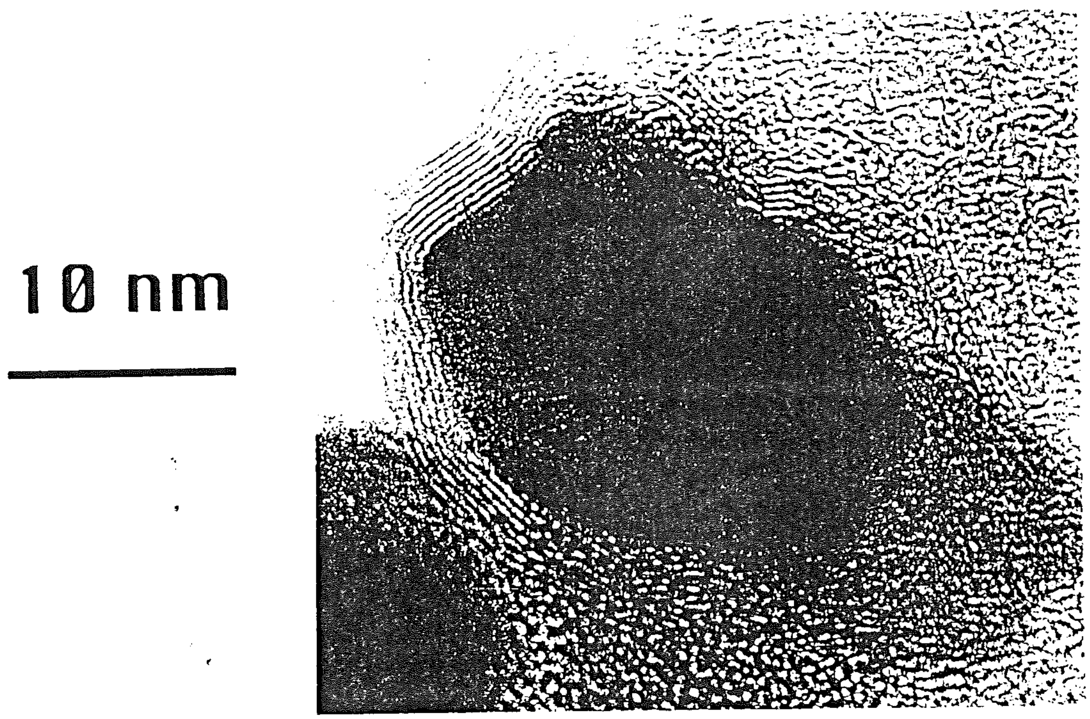

Figure 4 Co crystal encapsulated in layers of graphene sheets, produced with Co+W. The graphene layers seem to take the irregular shape of the Co particle, and there are several defects in the shell.

PROSPECT

The discovery of catalyst promoters provides a key to mass production of single-layer carbon nanotubes and metal encapsulated graphitic polyhedra. Nanotube properties and applications that depend on the diameter, such as electric conductivity[11], hydrogen storage media[12], and super strong materials may now be investigated. Catalytic production allows high efficiency and selectivity. Additional study of nanomaterials formed with various catalysts and promoters will help elucidate the growth dynamics, and many provide fundamental information that will further aid the development of potential applications.